REACTIVITY OF MILD GASIFICATION CHARS DERIVED FROM AN ILLINOIS COAL

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INTRODUCTION

In recent years, some emphasis has been given to producing premium liquids by mild gasification of coal[1-3]. The principle product from the mild gasification process is a partially devolatilized coal that must be effectively utilized (burned or gasified) to help the overall economics of the process. The loss of volatile matter indicates loss of hydrocarbon materials from the coal that can influence reactivity and combustion characteristics such as ignition, flame stability and carbon burn-out.

A large number of studies have been conducted on the oxidation reactivity and combustion properties of coal chars[4-6]. However, the majority of these studies have focused on chars prepared in laboratory reactors under rapid heating rates (10^4°C/sec). A few studies have dealt with the ignition[7] and reactivity of industrial process chars[8]. Reactivities of chars prepared under mild pyrolysis conditions have been recently reported[9]. Fuels prepared in laboratory reactors by heating coals at 12.5 to 20°C/min to 500°C were more reactive than either the parent coals or chars produced at higher pyrolysis temperatures. The present authors reported the reactivities of chars prepared from an Illinois coal under various pyrolysis conditions[10]. The results suggested that lower pyrolysis temperatures, higher heating rates, and shorter soak times increased reactivity.

In this paper, the reactivities and ignition temperatures of chars derived from an Illinois coal in a pilot scale reactor under mild gasification conditions are reported. The paper focuses on the influence of volatile matter and particle size on char reactivity.

EXPERIMENTAL

Char Preparation

Chars, also referred to as partially devolatilized (PD) coals, were produced in the Mild Gasification Unit at United Coal Company Research Corporation in Bristol, Virginia in October 1986. The coal was from the Illinois Basin Coal Sample Program, Sample IBC-103. The details of PD coal production have been reported elsewhere[11]. In brief, the PD coals were prepared by heating the coal under a slight vacuum in a fixed bed reactor (8-inch diameter, and 8-foot long) which was located inside a natural gas fired furnace. The furnace temperature was kept at 760°C during the production runs. Three PD coals designated as PD-1, PD-2, and PD-3 were prepared at residence times of 1.70, 2.90 and 3.17 hours.

Five size fractions of coals and PD coals were prepared by grinding the -8 mesh fuels in a rod mill. The crushed samples were dry sieved to obtain 65x100, 100x150, 150x200, 200x270, and 270x400 mesh fractions. The samples were stored under nitrogen to prevent oxidation.

Ignitability Tests

An ignitability test apparatus, shown in figure 1, was used to determine ignition temperatures of fuels. It consisted of an oxygen reservoir, a sample holder tube, a quartz reactor tube and an electric furnace. Fuel particles were injected into the reactor by oxygen gas through a built-in orifice. Six thin wire (0.0076 cm) type K thermocouples spaced at 2 cm apart measured axial temperature variations inside the reactor. The thermocouples were interfaced with a computer for automatic data collection. Typical data acquisition rates were six simultaneous measurements at 50 millisecond intervals.

In a typical ignition test, 20 mg of sample was injected into the preheated (between 390 and 500°C) reactor. The volume of oxygen carrier gas used to inject the sample was 10 cc at 5 to 7 psig. The relatively low pressure and volume of the carrier gas ensured that the fuel particles traveled with velocities approaching their free fall velocities inside the reactor.

Criteria for positive ignition were a brilliant flash and an abrupt increase in temperature inside the reactor during the test. If a negative test was noted, the reactor temperature was increased in 5°C increments and the test procedure was repeated.

Thermogravimetric Tests

An Omnitherm thermogravimetric analyzer (TGA) which was interfaced with a computer was used to obtain burning profiles (non-isothermal TGA) and isothermal reactivity data. Burning profiles were obtained by heating a sample mass of < 5 mg at a constant rate of 20°C/min in air to 850°C. A gas flow rate of 200 cc/min (STP) was used.

In isothermal reactivity tests, a sample mass of 2 to 4 mg was heated at 50°C/min under nitrogen flow to 550°C. The sample was then cooled to between 400 and 525°C and the nitrogen flow was replaced with dry air flowing at 200 cc/min. The weight of the char remaining, the rate of weight loss, and temperature were monitored by the computer at 5 to 40 second intervals depending on the reaction temperature. A modified TGA quartz furnace tube was used to obtain reliable rate data in the initial stage of oxidation[12]. The objective was to achieve the desired oxygen concentration in the furnace tube as quickly as possible.

Drop Tube Furnace Tests

These tests were conducted using the University of North Dakota Energy and Minerals Research Center drop tube furnace (DTF). The details of the furnace assembly, are given elsewhere[12].

Combustion tests were performed on the 65x100 and 270x400 mesh size fractions of the coal and three PD coals. The furnace temperatures selected were 900°C and 1300°C. The gas in the tube furnace (6.5 cm i.d.) contained 3% oxygen - 97% nitrogen and flowed at a nominal rate of 5 l/min. The flow rate was chosen to keep the residence times within a single furnace segment for nearly all the tests. The flow rate was adjusted to give residence times of 0.1 and 0.8 seconds. Carbon conversion efficiencies were calculated using the ash tracer method.

RESULTS AND DISCUSSION

Characterization of Fuels

The analyses of the coal and PD coals are summarized in tables 1 and 2. The volatile matter content, hydrogen and fixed carbon were nearly identical for the five size fractions of coal. However, for PD coals, volatile matter and hydrogen contents increased while carbon contents decreased with decreasing particle size range. The amount of volatiles increased from 24.8% to 29.2% for PD-1, from 15.7% to 21.3% for PD-2, and from 11.5% to 15.7% for PD-3 as particle size range decreased from 65x100 mesh to 270x400 mesh. Hydrogen content remained unchanged for PD-1 samples but increased by 21% for PD-2 and by 41% for PD-3 samples.

Comparison of the devolatilization profile (non-isothermal TGA under nitrogen atmosphere) of the fuels indicated that a major decomposition stage for the coal and PD coals occurred between 380 and 530°C[12]. The average weight losses were 25.6, 14.0, 7.4, and 4.8% for coal, PD-1, PD-2, and PD-3 respectively. These results confirmed the presence of varying amounts of coal-like materials in the PD-coals. This was attributed to the manner in which PD coals were prepared. Because the reactor was externally heated, the temperature at the wall of the reactor was much higher than at the center. Therefore, the coal particles near the wall were highly devolatilized whereas those at the center were not. The devolatilization profiles suggest that a fraction of coal was never devolatilized during processing.

Burning Profiles

Burning profiles obtained for the 65x100 mesh coal, PD-1, PD-2, and PD-3 coals are shown in figure 2. The profiles are offset to avoid overlap. The onset of burning was about 375°C for all the samples. However, there are clear differences among the burning profiles. Raw coal exhibited a single-burn profile, while double-burn profiles were observed for PD-1, PD-2 and PD-3. The second burn appeared as a shoulder peak for PD-1 and became more pronounced for PD-2 and PD-3. The double-burn behavior observed for the PD coals suggested the presence of at least two types of combustibles in the fuels. The two portions of combustibles burned in two distinct stages with peak burn rates at approximately 500°C and 550°C. The higher reactivity constituents (low temperature burn) had burning properties similar to coal and was present in larger concentrations in PD-1 followed by PD-2 and PD-3[12]. Fuels with higher volatile matter content burned more rapidly. For example at 500°C, the amount of combustible materials burned (not shown) was 70% for the raw coal, 55% for PD-1, 40% for PD-2, and 20% for PD-3. Differences in volatile matter had the greatest impact on burn-out temperatures which were 580, 630, 660 and 690°C for the coal, PD-1, PD-2 and PD-3. The results indicate that under the conditions used, raw coal was the most readily combusted fuel, followed by PD-1, PD-2 and finally PD-3.

Ignition Temperatures

The effect of volatile matter on ignition temperatures is presented in figure 3. Ignition temperatures varied between 406 and 494°C and were independent of volatile matter (except for 270x400 mesh fuels) in the range of 28 to 41% (daf). Below 28%, the volatile matter effect on ignition temperature appears to be significant among all the different particle size fractions tested (ignition temperature increased between 40 and 70°C). However, it has been shown in the literature that the role of volatile matter on the ignition temperature is little or none[7] (heterogeneous ignition

theory). Therefore, the differences in ignition temperatures observed could be attributed to inherent reactivity differences among the fuels tested.

The influence of particle size on ignition temperature is illustrated in figure 4. The particle size dependence of ignition temperature appeared to be rather mild with a spread of 30°C separating the studied size fractions. With the exception of the 65x100 mesh fraction (180μm average particle size), the ignition temperatures for the coal and PD coals increased with decreasing particle size. Ignition curves exhibited a minimum at 100x150 mesh size range (130μm).

The presence of a minimum on the ignition curves and the observed narrow temperature difference among different size fractions could be attributed to contributions of particle and cloud ignition. According to the Semenov thermal explosion theory[13], which is commonly used to model single coal particle ignition, large particles ignite at lower temperatures. However, it has been shown that under dust cloud conditions, ignition temperatures of fine particles are lower than those of large particles[14]. In this work, regardless of particle size range, a constant sample mass of 20 mg was used. Therefore, samples containing finer particles had higher solid mass density (mass/unit reactive volume) than those containing coarser particles, and the ignition approximated cloud ignition rather than particle ignition. As a result, there was a shift from dust cloud ignition to single particle ignition as particle size range increased. Because the opposite nature of these two mechanisms offset the other, a minimum and a narrow temperature difference were observed for ignition curves of the fuels.

Isothermal Reactivity Studies

Initial reactivity tests were conducted at 475°C. The data were used to calculate apparent rate, R,

$$R = \frac{-1}{f} \frac{df}{dt} \qquad (1)$$

and

$$f = (M-M_a)/(M_o-M_a) \qquad (2)$$

where f = fraction combustible remaining at time t, M = mass of sample at time t, M_o = initial sample mass, M_a = mass of sample at complete conversion, i.e. ash. At 475°C, the rates were the same for all particle sizes, indicating the data were obtained under diffusion-free conditions. The apparent rates at 50% conversion were 0.013, 0.025 and 0.062 g/g/min for PD-1, PD-2 and PD-3, respectively. The rate for a char (18% volatile matter) that was prepared in the TGA at 500°C under nitrogen atmosphere was 0.2 g/g/min.

Additional tests were performed at temperatures between 400 to 525°C to evaluate activation energies for the oxidation of 200x270 mesh fuels. In figure 5, the values of ln(-df/dt/f) evaluated at 50% burn-off are plotted against 1/T. The activation energies obtained from the slopes of the plots were 146, 137, 134, and 125 kJ/mole for the 500°C char, PD-1, PD-2 and PD-3. The observed activation energies are comparable with previously reported values for various types of coal chars[8,9]. The data shown in figure 5 indicate that the 500°C char is 2.5, 6.2, and 9.5 times more reactive than PD-1, PD-2, and PD-3.

Drop Tube Furnace Tests

Figure 6 shows carbon conversion at 900°C for 0.1 and 0.8 second residence times for 65x100 mesh and 270x400 mesh size fractions of coal and PD coals. Carbon conversions ranged from 10 to 28% at 0.1 second residence time and from 10 to 75% at 0.8 seconds residence time as volatile matter content increased from 12 to 40% (daf basis). These data indicate that 1) the fraction of carbon burned increased with increasing volatile matter, with a larger increase noted at 0.8 seconds, and 2) the effect of residence time on carbon loss was more pronounced for fuels with higher volatile matter content. The particle size effect on carbon conversion was small, although it was more pronounced at longer residence times.

Carbon conversion data at 1300°C are shown in figure 7. Carbon conversion increased with increasing volatile matter and increasing residence time. The data indicate that the effects of volatile matter and residence time on carbon conversion were more pronounced at the higher furnace temperatures. The percent of carbon combusted at 1300°C and 0.8 second residence time varied between 62 and 90 for the 65x100 mesh size fractions and between 72 and 99 for the 270x400 size fractions as volatile content of fuels increased from 10.5 to 40% (daf basis). Data also revealed that carbon conversion curves at 1300°C and 0.1-second were almost identical to those at 900°C and 0.8 second. This observation indicates that temperature and residence time are interrelated.

The DTF data suggest that variables which had significant influence on the combustion efficiency were temperature and residence time, followed by fuel type (volatile matter) and particle size. Statistical analyses of the test data indicated that: 1) there was no interaction between volatile matter and any other variable, and 2) external particle surface area was a contributing factor. This indicates that at high combustion temperatures, burning rates were partially controlled by the external mass transfer rate. Finally, DTF data revealed similar trends in reactivity as that obtained with the TGA method.

CONCLUSIONS

Fuels used in this study consisted of a mixture of highly devolatilized coal and relatively unheated coal with the proportion of each depending on the overall volatile matter content. Burn-out temperature and ignition temperatures increased significantly with decreasing volatile matter below 28%. High-temperature drop tube furnace tests revealed that temperature and residence time affected combustion efficiencies most, followed by fuel volatile matter content and particle size.

ACKNOWLEDGEMENTS

This work was funded inpart by grants from the Illinois Coal Development Board through the Center for Research on Sulfur in Coal.

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Table 1. Analyses of coal*, wt% (dry basis)

Volatile Matter	39.2	Hydrogen	4.9
Fixed Carbon	52.4	Carbon	73.8
H-T Ash	8.4	Nitrogen	1.7
BTU/lb	13437	Oxygen	8.7
Moisture	5.4	Sulfur	2.3
		Chlorine	.2

*Illinois hvBb coal. Predominantly Springfield (No. 5), 20% Herrin (No. 6) blended at washing plant.

Table 2. Characterization data for chars

Particle size, mesh	65x100	100x150	150x200	200x270	270x400
PD-1					
volatile matter	24.8	24.6	25.7	27.8	29.2
fixed carbon	75.2	75.3	74.3	72.2	70.8
hydrogen	3.9	3.9	3.9	4.0	4.0
PD-2					
volatile matter					
carbon	15.7	15.9	17.3	19.5	21.3
hydrogen	84.2	83.8	82.7	79.9	78.7
	2.5	2.7	2.8	2.9	3.1
PD-3					
volatile matter	11.5	11.7	12.4	13.7	15.7
carbon	88.5	88.3	87.5	85.5	84.2
hydrogen	1.8	1.9	2.0	2.2	2.5

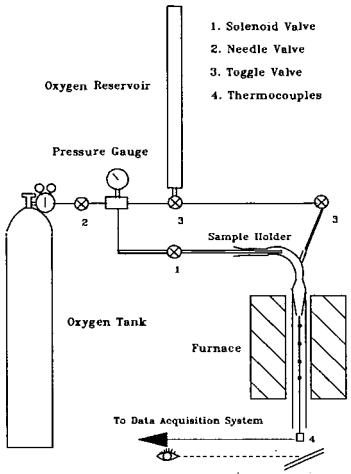

Figure 1. Ignitability test apparatus

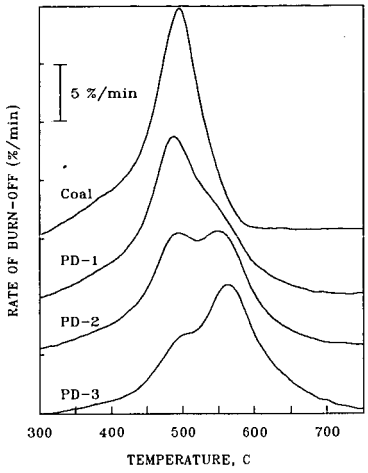

Figure 2. Burning profiles for coal and PD coals

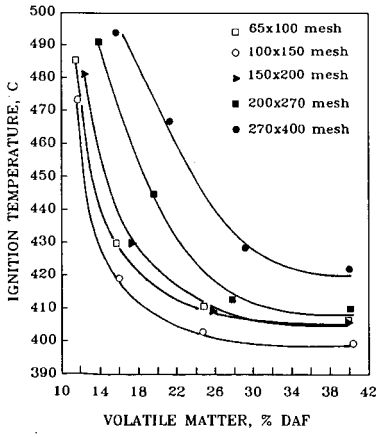

Figure 3. Effect of volatile matter on ignition temperature.

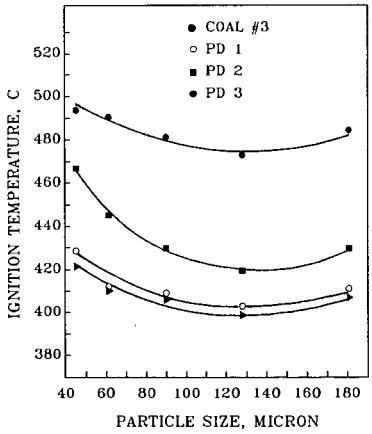

Figure 4. Effect of particle size on ignition temperature.

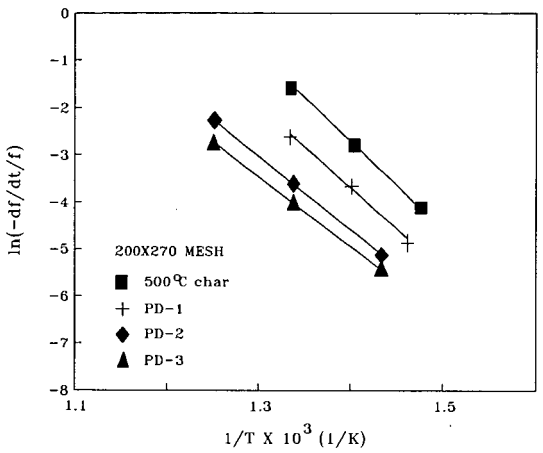

Figure 5. Ahhrenius plot from isothermal TG data for 200x270 mesh fuels.

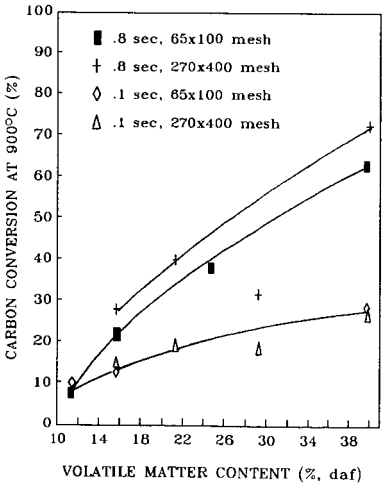

Figure 6. Effect of volatile matter content on carbon conversion in the drop tube furnace at 900° C.

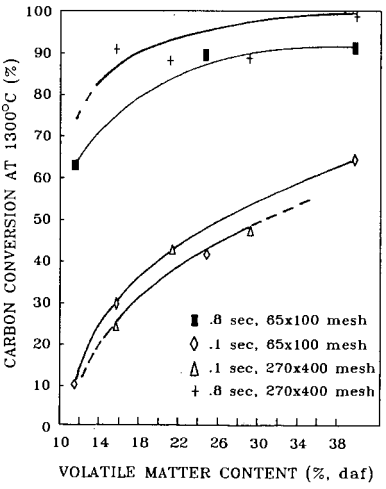

Figure 7. Effect of volatile matter content on carbon conversion in the drop tube furnace at 1300° C